Electronic Supplementary Information

CO$_2$-triggered fine tune of electrical conductivity via tug-of-war between ions

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Materials and Methods

Materials

3-Bromopropylamine hydrobromide and phthalaldehydic acid were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. 1-Methylimidazole was purchased from Acros Organics and used as received. Methanol, ethyl acetate, tetrahydrofuran (THF), dichloromethane, acetic acid, sodium hydroxide was purchased from Kanto Chemical Co., Inc. and used as received. Amberlite IRN 78A and alminum oxide was purchased from Sigma-Aldrich Co., Llc. and used as received.

Synthesis of $[\text{C}_3\text{NH}_2\text{mim}]^+\text{[o-aldBzCOO]}$

1-Methylimidazole (10.9 g, 133 mmol) was dissolved in 80 mL THF, and then 3-bromopropylamine hydrobromide (30.6 g, 140 mmol) was added to the solution under argon atmosphere. The mixture was refluxed at 90 °C for 5 h. After removing solvent, the solid was recrystallized in methanol/ethyl acetate mixture several times and dried under reduced pressure. The bromide anion was converted to hydroxide anion by stirring the bromide salt aqueous solution with Amberlite IRN 78A. After filtration, resulting liquid was neutralized by phthalaldehydic acid and then dried in vacuo. The resulting solution diluted with dichloromethane solution was passed through a column filled with aluminium oxide to remove excess amount of phthalaldehydic acid. The resulting solution was dried in vacuo. After drying, $[\text{C}_3\text{NH}_2\text{mim}]^+\text{[o-aldBzCOO]}$ was obtained as the ZI form.
$^1$H NMR (400 MHz; DMSO-$d_6$; Me$_4$Si) δ = 9.62 (s, 1H, NCHN), 8.86 (s, 1H, N=CHC), 7.90 and 7.69 (t, $J$ = 1.6 Hz, 2H, NCHCHN), 7.65-7.13 (m, 4H, protons of aromatic ring), 4.19 (t, $J$ = 6.2 Hz, 2H, NCH$_2$CH$_2$CH$_2$N=CH), 3.81 (s, 3H, NCH$_3$), 3.41 (t, $J$ = 5.7 Hz, 2H, NCH$_2$CH$_2$CH$_2$N=CH), 2.26-2.06 (m, 2H, NCH$_2$CH$_2$CH$_2$N=CH). $^{13}$C NMR (100 MHz; chloroform-$d$; Me$_4$Si) δ = 170.22, 138.29, 134.33, 129.69, 128.89, 127.36, 126.36, 124.22 122.75, 56.75, 49.10, 46.87, 36.09, 30.39. Elemental analysis: [C$_3$NH$_2$ mim][o-aldBzCOO]·2.2H$_2$O (Found: C, 58.0; H, 6.6; N, 13.2. Calc. for C$_{15}$H$_{21.4}$N$_3$O$_4$: C, 58.0; H, 6.9; N, 13.5%).

**Structural shift of [C$_3$NH$_2$ mim][o-aldBzCOO]**

[C$_3$NH$_2$ mim][o-aldBzCOO] (1.0 wt%) was added to ultrapure water. The pH of the solution was changed with 33 wt% NaOH solution and 25–100 wt% acetic acid solutions. The ratio of the IL form was confirmed by $^1$H NMR. N$_2$ and CO$_2$ gas was saturated by water before passing the sample solutions to prevent evaporation of water of the samples; we confirmed that the volume of the sample solutions did not changed before and after long-time gas bubbling.

**Measurement of electrical conductivity of [C$_3$NH$_2$ mim][o-aldBzCOO] solution**

An electrical conductivity meter (LAQUA DS-72, Horiba Ltd.) was used for the measurement of electrical conductivity of the aqueous solution of [C$_3$NH$_2$ mim][o-aldBzCOO]. The measurement was carried out after the 1.0 wt% solutions were bubbled
with N\textsubscript{2} or CO\textsubscript{2} until the electrical conductivity did not shift. N\textsubscript{2} and CO\textsubscript{2} gas was saturated by water before passing the sample solutions to prevent evaporation of water of the samples. The partial pressure of CO\textsubscript{2} was controlled using a controlling system (Multi-GAS 3000, Tai-tec corporation), by mixing with air.

**Observation of emission from light-emitting diode (LED) incorporating a [C\textsubscript{3}NH\textsubscript{2}mim][o-aldBzCOO] solution as a variable resistor**

The electronic circuit was prepared with a LED (HK-LED 5H(R), Asahi Electric CO. Ltd.), an alternating-current source (GW instek APS-7050, Texio Technology Corporation), and an ammeter (MT-4510, Mother tool Co. Ltd.). The 1.0 wt% [C\textsubscript{3}NH\textsubscript{2}mim][o-aldBzCOO] aqueous solutions (3 mL) were bubbled with 0.1 kPa of CO\textsubscript{2} for 20 sec. After LED was electrified (3.5 V, 45 Hz), the current value was measured and a picture was taken immediately. The same procedure was successively carried out with 1 and 101 kPa of CO\textsubscript{2}. After that, the same procedure was conducted with N\textsubscript{2} for 16h. When the emission was controlled by exhaled breath, bubbling the breath was conducted for 3 min.
Supporting Figures
pH 6.5

Measured with co-axial tubes
inner tube: DM5O-\text{d}_6
outer tube: sample

pH 7.5

Measured with co-axial tubes
inner tube: DM5O-\text{d}_6
outer tube: sample
Fig. S1. $^1$H NMR spectra of 1 wt% [C$_3$NH$_2$mim][o-aldBzCOO] aqueous solution before and after changing pH by acid/base.
Fig. S2. $^1$H NMR spectra of 1 wt% $[\text{C}_3\text{NH}_2\text{mim}][\alpha\text{-aldBzCOO}]$ aqueous solution after bubbling with (top) N$_2$ and (bottom) CO$_2$. 
We subjected \([C_{3NH2}mim][o-aldBzCOO]\) solution to mass spectrometry before CO\(_2\) bubbling (Fig. S3a, b). Two small and large peaks were observed and attributed to the cation of the IL form (m/z=140) and ZI form (m/z=272) in positive mode because \([C_{3NH2}mim][o-aldBzCOO]\) is a mixture of IL- and ZI form. ZIs are generally observed in mass spectra as proton-adducted form in positive mode because ZIs have single positive and negative charges and thus they are neutral in charge. Two large and small peaks were observed and attributed to the anion of the IL form (m/z=149) and ZI form (m/z=270, proton-abstracted form) in negative mode.

While the same peaks (m/z=140 and 272 in positive mode, m/z=149 and 270 in negative mode) were found after CO\(_2\) bubbling (Supplementary Fig. S3c, d), but the peak height was different: the peak of IL form was higher than that of ZI form. This result clearly shows the exact structures of IL- and ZI forms and they shifted by bubbling with CO\(_2\).

Some amines and ILs have ability to capture CO\(_2\) via covalent bond. Then we have subjected the 1 wt\% \([C_{3NH2}mim][o-aldBzCOO]\) soluiton to mass spectrometry after CO\(_2\) bubbling (Fig. S3c). If the cation reacts with CO\(_2\), the peak at 184 in m/z appears. However, no peak was observed at 184 and it shows the cation does not react with CO\(_2\). This strongly supports that CO\(_2\) does not react with \([C_{3NH2}mim][o-aldBzCOO]\) and consequently CO\(_2\) works simply as an acid (H\(_2\)CO\(_3\)) in the solution.
Fig. S3. Mass spectra (a, c: positive mode, and b, d: negative mode) of 1 wt% \([C_3NH_2\text{mim}][o-\text{aldBzCOO}]\) aqueous solution (a, b) before and (c, d) after \(CO_2\) bubbling.
Fig. S4. A picture of the system for the emission experiment. The top right vial contains a \([\text{C}_3\text{NH}_2\text{mim}][\text{o-aldBzCOO}]\) solution. \(\text{CO}_2\) and \(\text{N}_2\) flowed from gas cylinders to the solution through the top right syringe. Nothing is inside the center box except for conducting wires (the box is used just for fixing the LED).